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Supporting Information
Carbon supported Olivine type phosphate framework: a promising electrocatalyst for sensitive detection of dopamine

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1. Synthesis and crystal growth

The $LiMnPO_4$ single crystals were prepared by the traveling solvent floating zone (FZ) method and the flux growth technique. For FZ method, initially, the $LiMnPO_4$ polycrystalline sample was prepared by standard solid reaction method. The stoichiometric amounts of Li_3PO_4 (Chempur 99.99 %), $MnCO_3$ (Aldrich 99.99 %) and $NH_4H_2PO_4$ (Chempur 99.99 %) were ground together carefully to homogeneity in an agate mortar and sintered in alumina crucible several times for 48 hours at 800 °C in Ar atmosphere with intermediate grinding until a single phase $LiMnPO_4$ sample was obtained. The final single phase of $LiMnPO_4$ sample is in an orange-white color. The obtained pure powder sample was pressed into rods shape polycrystalline sample using hydrostatic pressure and then again sintered for 34 h at 800 °C. The four 300 W air-cooled halogen lamps were employed. A quartz tube with 4 mm wall thickness was used as the growth chamber. The applied Ar pressure in the growth chamber was 3 bar. The feed rod was rotated clockwise at a rate of 12 rpm, and the seed anticlockwise 12 rpm. The growth rate was 1.5 mm/h.On the other hand, LiCl was used as the flux for flux growth of the $LiMnPO_4$ single crystal. The stoichiometric mixer of high purity $MnCl_2$ (99.999% Aldrich) and Li_3PO_4 (99.999% Aldrich), and the flux LiCl were placed in an alumina crucible (Mixture and flux LiCl ratio was AA: BB). Then the crucible was placed into the furnace and heated to 800 °C. Further, the temperature 800 °C was maintained for 24 hours to get homogeneous melt. The furnace was allowed to cool slowly to 600 °C at a rate of 1 °C/h and then cooled to room temperature at a rate of 70 °C/h. Finally, pink in color of the $LiMnPO_4$ single crystal was obtained. Finally, pink in color of the $LiMnPO_4$ single crystal was obtained.

2.X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) was employed to study the chemical state of LiMnPO4/f-MWCNTs composite. The XPS spectrum is shown in Fig.3 (a) indicates the existence of principal elements peaks, such as Li, Mn, and P along with traces of the oxygen element. The P 2p spectrum of the working electrode used to displays two components due to spin-orbit coupling (2p3/2 and 2p1/2 separated by ~0.9 eV), it is observed that there is a single peak at 133.9 eV. The observation of only one P 2p peak is associated to the phosphate (PO4)3- ion of LiMnPO4/f-MWCNTs. The core level spectrum of Mn 2p shown in Fig.3 (f). The Mn 2p spectrum consisted of two major peaks corresponding to Mn 2p3/2 and Mn 2p1/2, respectively.1 The peak positions at the binding energy of 644 eV (2p3/2) and 655 eV (2p1/2) are related to the +2 oxidation state of Mn. Fig.3 (d) shows that the C 1s core level spectrum with the binding energy 287.3 eV belongs to C=O groups from carbon. The O 1s spectrum of the starting electrode displays a narrow peak at 531.4 eV, which is attributed to oxygen atoms of the (PO4)3- phosphate ion of LiMnPO4/f-MWCNTs composite. The observed results are in agreement with the earlier report .2, 3

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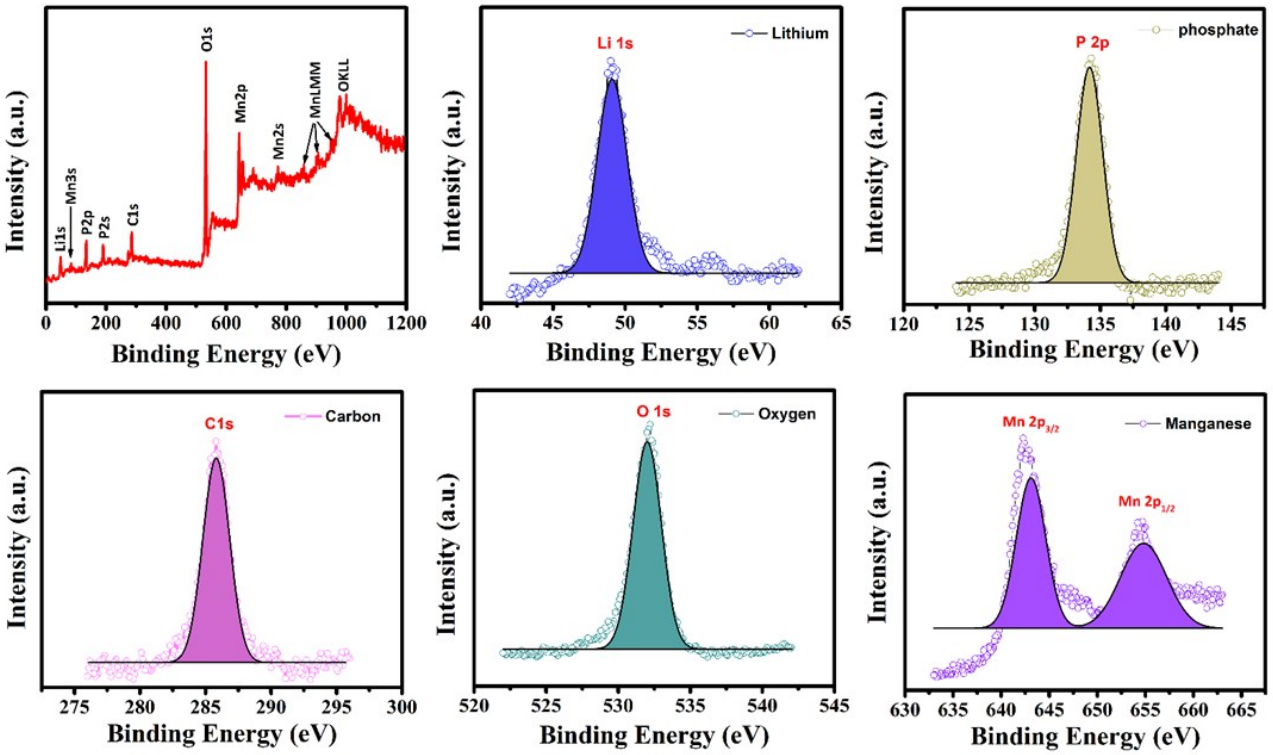

Fig.S1. (a) XPS survey-scan spectrum of *LiMnPO$_4$/f-MWCNTs* composite, (b) high resolution spectrum of Li1*s* (c) P2*p*, (d) C1*s*, (e) O1*s* and (f) Mn2*p*.

3. Magnetism of $LiMnPO_4$

The χ(T) increases with a decrease in temperature and attained a broad maximum at 37 K which is a characteristic feature of low-dimensionality. χ(T) decreases with a further decrease in temperature. The first derivative of susceptibility (dχ(T)/dT) exhibits a sharp peak at 33 K which correspond to a long-range AFM transition. At high temperature (T>100), the χ(T) data can be fitted with the Curie-Weiss law [χ(T) = C/(T − θ)] satisfactorily. The fit yields μeff = 6 μB which is well agreed with the spin-only value of Mn2+ (5.9 μB) and Weiss temperature θ = −63 K. The negative Weiss temperature indicates an antiferromagnetic coupling between Mn ions. The strongest exchange interaction occurs by Mn-O-Mn bond in the b-c plane. The super-super exchange interaction occurs through Mn-O-P-O-Mn in the interlayer magnetic coupling.

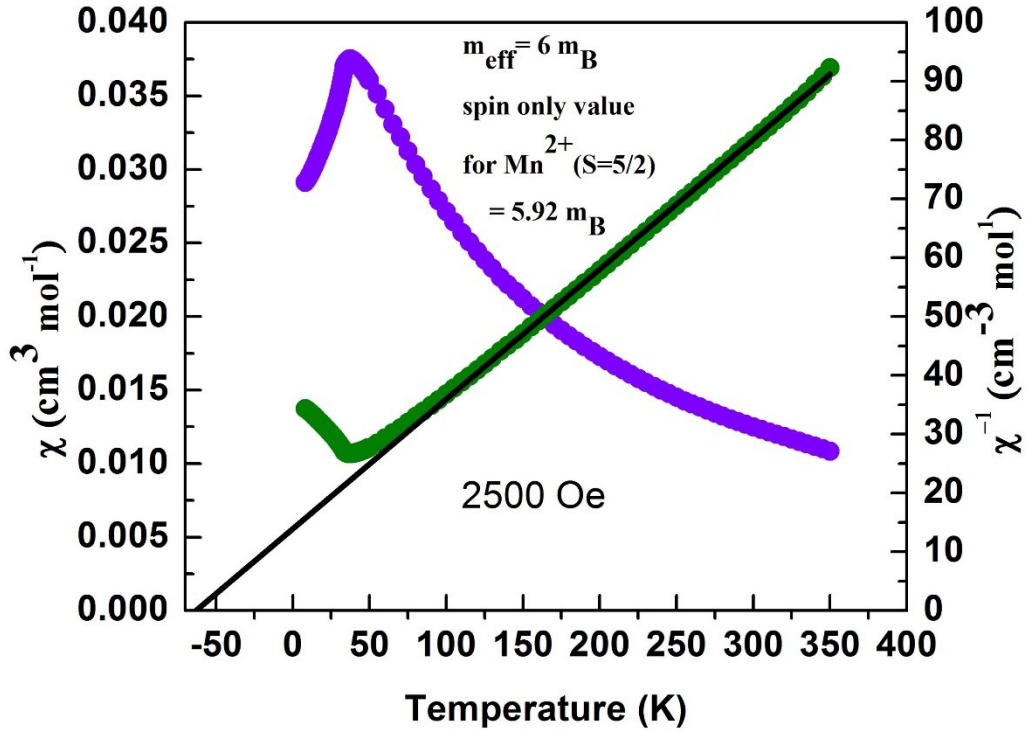

Fig.S2 (a) shows the temperature dependence of magnetic susceptibility χ(T) and the corresponding inverse susceptibility measured at an applied magnetic field of 2500 Oe in the temperature range between 8 and 350 K.

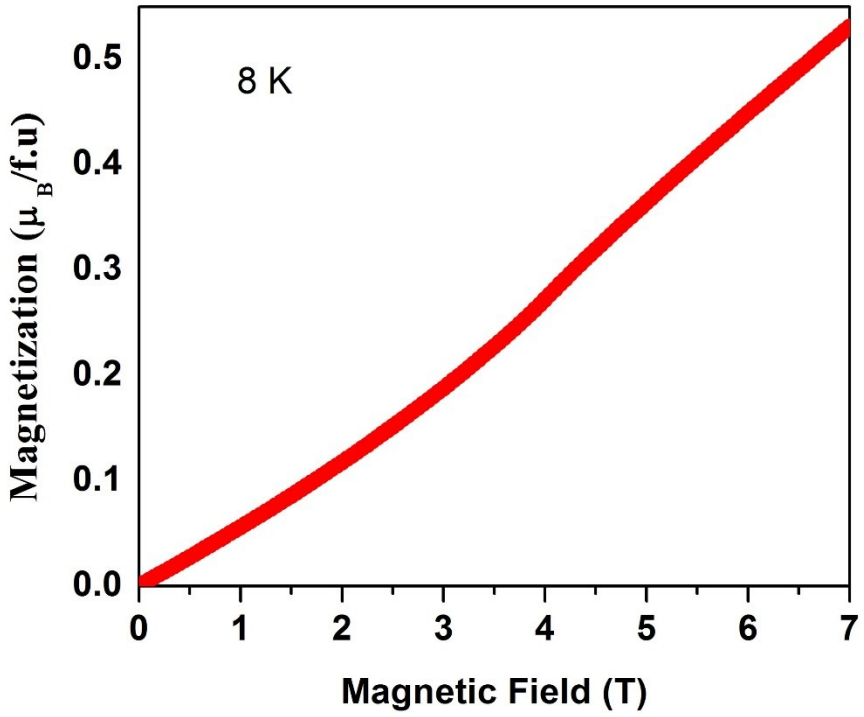

Fig.S3 (b) depicts the magnetization versus magnetic field up to 7 T at 8 K. The magnetization curve varies nonlinearly with applied magnetic field, suggesting spin-flop transition occurs at 4 T.

4.Optimization

The optimization studies are more important and it may directly affect the electrochemical behavior of DA. Hence, the optimization drop coating amount of LiMnPO4/f-MWCNTs composite towards the detection of 50 µM DA was investigated by CV. The optimization result is shown in Fig. S7. The 6µL drop coated LiMnPO4/f-MWCNTs composite modified electrode showed a maximum current response for DA than that of other drop coated electrodes. Hence, 6µL drop coated LiMnPO4/f-MWCNTs composite modified electrode was used as an optimum quantity for further electrochemical investigations.

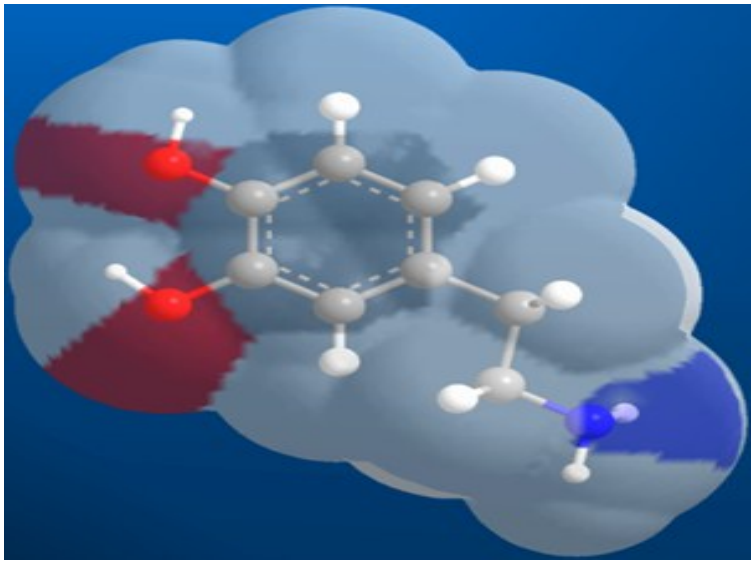

Fig S4 The 3D structural view of the DA. (IUPAC Name: 4-(2-aminoethyl) benzene-1,2-diol)

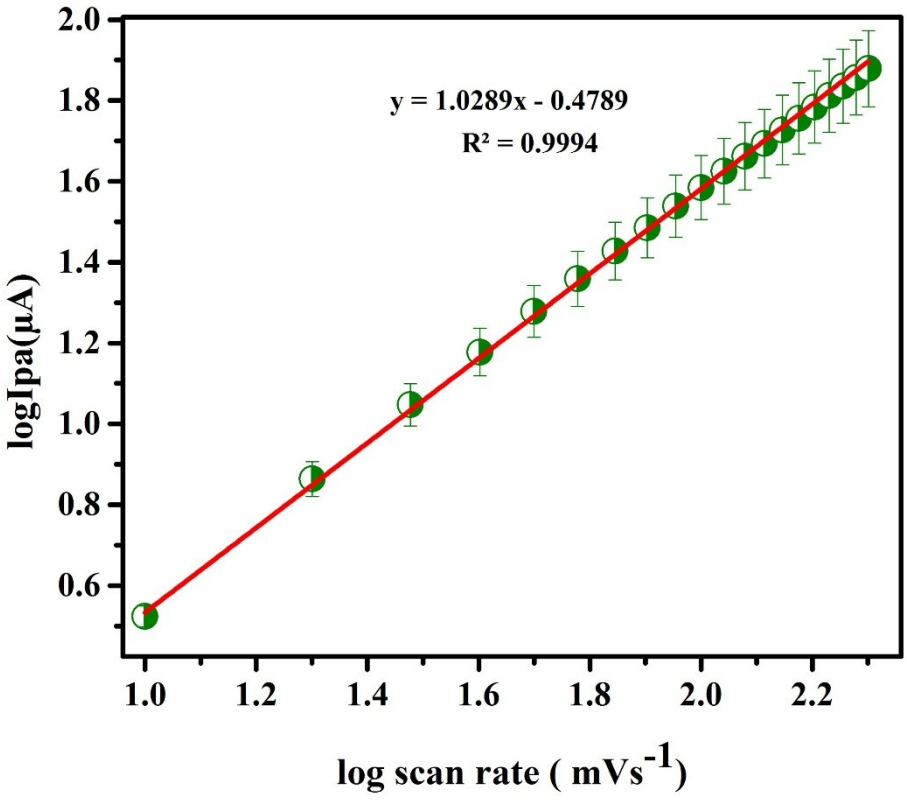

Fig S5. The logarithmic plot of scan rate versus log (Ipa)

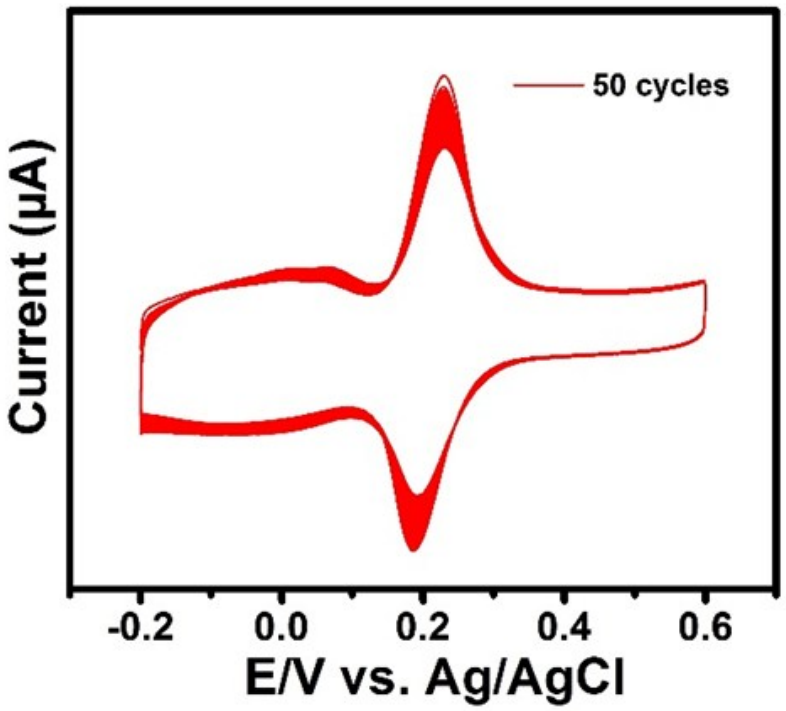

Fig.S6 The sensing performance of LiMnPO4/f-MWCNTs composites recorded continuously up to 50 cycles.

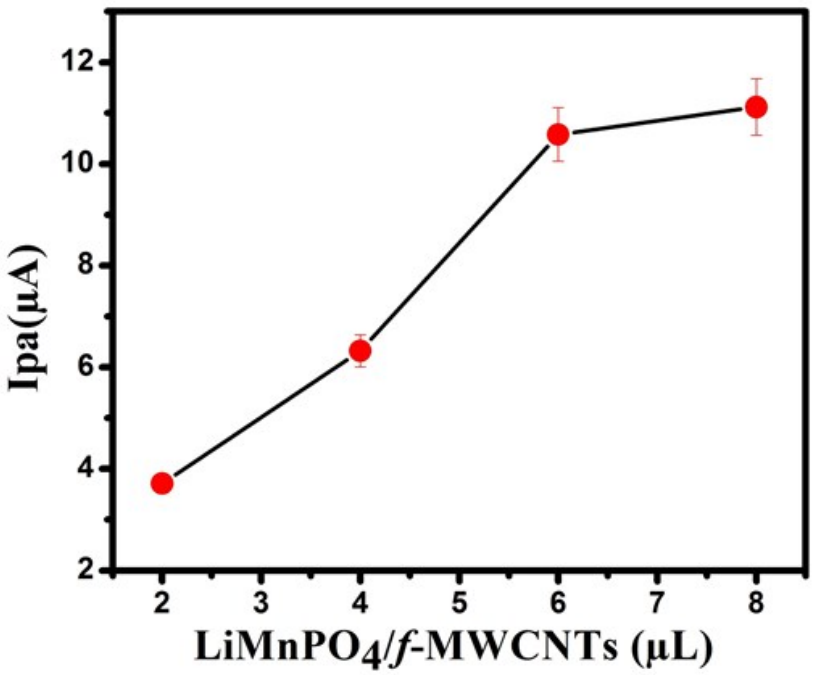

Fig.S7. The CV response for different drop coated LiMnPO4/f-MWCNTs composite in 50 μM DA at a scan rate of 50 mV s-1.

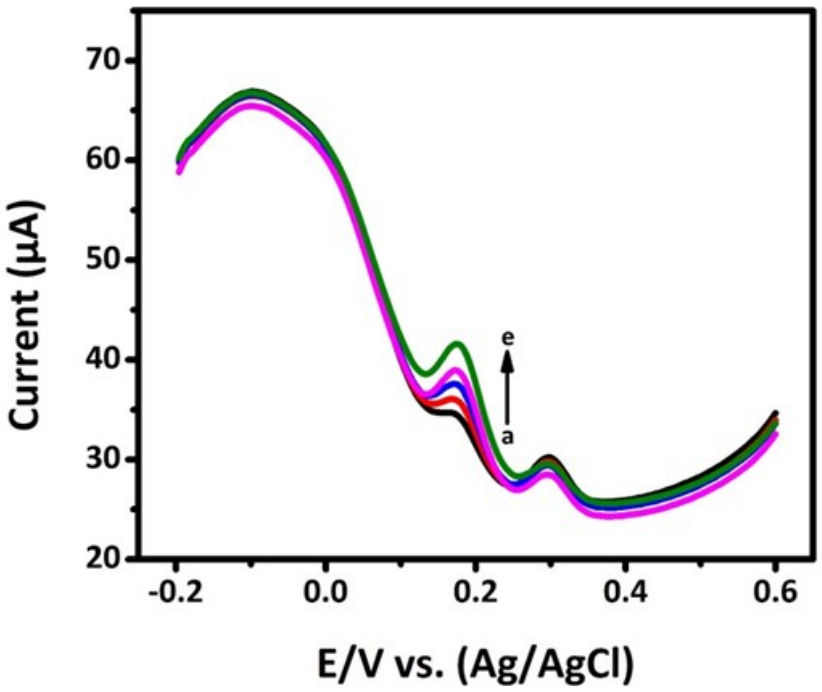

Fig S8. DPV response of GCE/LiMnPO4/f-MWCNTs modified electrode in the presence of 0.05 M PB solution containing real samples at different concentration (0.001 M) of DA for Human serum sample at different concentration of DA (a) 10, (b) 20, (c) 30, (d) 40, (e) 50.

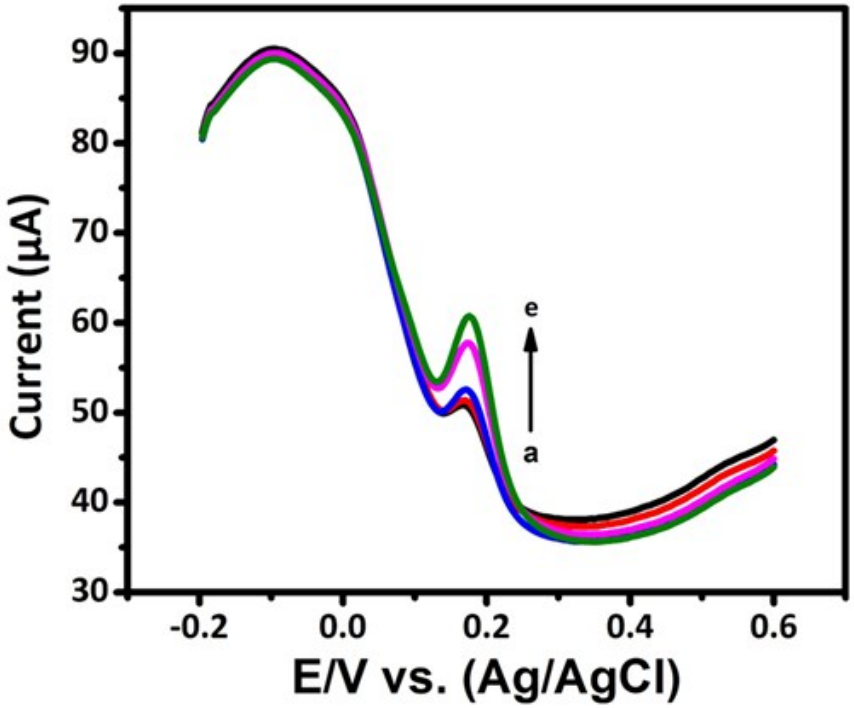

Fig 9. DPV response of GCE/LiMnPO$_4$/*f*-MWCNTs modified electrode in the presence of 0.05 M PB solution containing real samples at different concentration (0.001 M) of DA for rat brain sample at different concentration of DA (a) 10, (b) 20, (c) 30, (d) 40, (e) 50.

Tabulation

Table 1. The binding energy of detected elements and assignation of materials determined by XPS

Photoelectron	C-$LiMnPO_4$		Assignation
	Binding energy/ eV	State ratio/ at. %	
C 1*s*	287.3	13.8	C=o
O 1*s*	531.4	46.8	C=O, Metal-O, PO_x Li_xO_y, Li_xPO_y PO_x Mn_xO_y
Li 1*s*	55.3	19.0	
P 2*p*	133.9	12.4	
Mn 2*p*3	642.9	8.0	

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